Untwisting of a Cholesteric Elastomer by a Mechanical Field

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A mechanical strain field applied to a monodomain cholesteric elastomer will unwind the helical director distribution. There are similarities with the classical problem of an electric field applied to a cholesteric liquid crystal but also differences. Frank elasticity is of minor importance unless the gel is very weak. The interplay is between the director being helically anchored to the rubber elastic matrix and the external mechanical field. Stretching perpendicular to the helix axis induces the uniform unwound state via the elimination of sharp, pinned twist walls above a critical strain. Unwinding through conical director states occurs when the elastomer is stretched along the helical axis.

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Monodomain cholesteric elastomers are formed by cross-linking mesogenic chiral polymers in the cholesteric state with a properly formed helical director twist. The subsequent retention of the helical state as an elastic equilibrium [1] is a natural consequence of topological imprinting of textures in the cross-linked network, seen in a number of other elastomers with liquid crystalline order and other microstructure. Recently an interesting aspect of chiral imprinting was established by cross-linking nematic polymers in a chiral state purely induced by a chiral solvent [2]; on removal of the solvent, the network of chemically achiral nematic chains remains macroscopically cholesteric. Such an imprinting was envisaged a long time ago [3] on phenomenological grounds. It is now important to consider the mechanical possibilities of such solids with a helical microstructure, expecting new transitions and instabilities characteristic of liquid crystalline elastomers. Additionally there are obvious device applications of such materials, which combine all the optical properties of twisted nematic liquids with the remarkable mechanical characteristics of rubbers. There is some experimental evidence [4] that such effects are indeed observable and our hope is that this theoretical work will stimulate more studies in this field.

Consider a monodomain cholesteric elastomer with an ideal helically twisted director $\mathbf{n}_0(z)$ in the xy plane, initially making angle $\phi_0 = q_0 z$ with the x axis (Fig. 1). We shall examine two specific cases of imposed uniaxial extension: (i) the transverse deformation $\lambda_{xx} = \lambda$, in the plane including $\mathbf{n}_0$, and (ii) the longitudinal deformation along the helix axis $\lambda_{zz} = \lambda$.

The symmetry obvious from Fig. 1 requires that in the case (i) the director remains in the xy plane, characterized by the azimuthal angle $\phi(z)$, while in the case (ii) one may expect a conical texture with $\mathbf{n}(z)$ inclined towards the stretching axis z and, therefore, described by two angles θ and ϕ (cf. Fig. 3 below). In ordinary liquid cholesterics subjected to, e.g., a magnetic field H_z, such conical states are not generally seen, preempted by the 90° switching of the helix axis and then untwisting in the "transverse" geometry [5]. We shall see that in elastomers, due to the chiral imprinting, this regime is not possible and the conical director configurations should occur.

An elastic material with a microstructure represented by an independently mobile director orientation is analogous to a Cosserat medium. In the limit of linear elasticity the relative rotation coupling between the director rotation $\boldsymbol{\omega} = [\mathbf{n} \times \delta\mathbf{n}]$ and the antisymmetric part of strain, $\Omega_{\mathrm{i}} = \epsilon_{ijk}\varepsilon_{jk}$,

$$\frac{1}{2} D_1[\mathbf{n} \times (\boldsymbol{\Omega} - \boldsymbol{\omega})]^2 + D_2 \mathbf{n} \cdot \underline{\underline{\varepsilon}}^{(s)} \cdot [\mathbf{n} \times (\boldsymbol{\Omega} - \boldsymbol{\omega})], \tag{1}$$

was first written down phenomenologically by de Gennes [6], $\underline{\underline{\varepsilon}}^{(s)}$ being the symmetric part of the small strain defined as $\underline{\underline{\varepsilon}} = \underline{\underline{\lambda}} - \underline{\underline{\delta}}$. This symmetry-based expression is valid only for small deformations, having only linear and quadratic terms in the local relative rotation.

The microscopic statistical-mechanical theory of nematic rubber elasticity, e.g., [7], obtains a generalization of the classical rubber-elastic energy density in the form of a frame-independent expression

$$F = \frac{1}{2}\,\mu \mathrm{Tr}(\underline{\underline{\ell}}_0 \cdot \underline{\underline{\lambda}}^T \cdot \underline{\underline{\ell}}^{-1} \cdot \underline{\underline{\lambda}}), \tag{2}$$

plus the constraint of material incompressibility, expressed by the condition $\mathrm{Det}(\underline{\underline{\lambda}}) = 1$ on the strain tensor. Apart

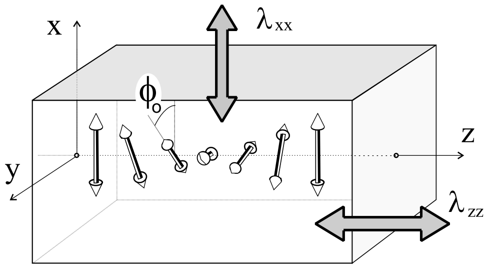

FIG. 1. The initial director $\mathbf{n}_0(z)$ in a cholesteric helix makes an azimuthal angle $\phi_0 = q_0 z$ with the x axis; the helical pitch is $p = \pi/q_0$. Two principal directions of mechanical deformation, λ_{xx} and λ_{zz}, are shown by arrows.

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from the strain tensor, the other entries in Eq. (2) are $\underline{\underline{\ell}}_0 = \ell_\perp \underline{\underline{\delta}} + (\ell_\| - \ell_\perp)\mathbf{n}_0\mathbf{n}_0$ and $\underline{\underline{\ell}}^{-1} = (1/\ell_\perp)\underline{\underline{\delta}} + (1/\ell_\| - 1/\ell_\perp)\mathbf{nn}$, the reduced shape and inverse shape tensors characterizing the Gaussian distribution of nematic polymer chains before and after the distortion $\underline{\underline{\lambda}}$. The shear modulus $\mu = n_s k_B T$ (with n_s the number density of network strands, proportional to the cross-link density) characterizes the underlying isotropic rubber and sets the energy scale of distortions. The free energy density Eq. (2) is valid up to large strains and correctly predicts the optomechanical responses and the soft elasticity of nematic elastomers. The free energy F is a function of only the chain anisotropy $r = \ell_\| / \ell_\perp$, the ratio of the effective step lengths parallel and perpendicular to the director. It can be independently measured from neutron scattering or from spontaneous mechanical distortions ongoing from the nematic to isotropic phase. Unless there is a large nematic order change induced by $\underline{\underline{\lambda}}$, the shape $\underline{\underline{\ell}}$ is essentially just a rotated version of $\underline{\underline{\ell}}_0$, a uniaxial ellipsoid with the long axis (at $r > 1$) oriented along $\mathbf{n}$ instead of $\mathbf{n}_0$.

Embedded in the general expression Eq. (2) is the penalty for local director deviations from the orientation $\mathbf{n}_0$ imprinted into the network at formation. When no elastic strains are allowed, this elastic energy reduces to

$$F = \frac{3}{2}\mu + \frac{1}{2}\mu\frac{(r-1)^2}{r}\sin^2\theta\,, \tag{3}$$

where θ is the local angle between $\mathbf{n}$ and $\mathbf{n}_0$. The elastic penalty for such a deviation, appropriately proportional to the square of chain anisotropy, is the coefficient D_1 of the de Gennes phenomenological expression at small deformations, Eq. (1). This has to be compared with the Frank elastic penalty for director curvature deformations, $\frac{1}{2}K(\nabla\mathbf{n})^2$. The length scale $\xi \sim \frac{1}{r-1}\sqrt{K/\mu}$ at which the two energy contributions are comparable is usually small: $\xi \sim 10^{-8}$ m for a typical $K \sim 10^{-11}$ J/m, $\mu \sim 10^5$ J/m^3 and not too small anisotropy, r. This is rather less than the cholesteric pitch p, which is a characteristic scale in our problem. Therefore, the anchoring of the director $\mathbf{n}$ to the rubbery matrix, described by Eq. (2), tends to dominate over Frank effects.

We shall assume that a cholesteric elastomer is locally like a nematic in its elastic response: rubber elasticity is determined on the scale of network cross-link separations (a few nanometers), whereas cholesteric pitches are 10^3 times longer. We can at once see why the chiral structure is stable but how mechanical fields can destabilize it. With no elastic strain, the free energy penalty is $\sim\frac{1}{2}D_1(\phi - \phi_0)^2$ for rotating the director away from its original helical texture $\phi_0 = q_0 z$. On the other hand, if strains are applied, the rubber can lower its elastic energy Eq. (2) by rotating the director $\mathbf{n}$ towards the axis of principal extension. This general principle of adjusting the microstructure to minimize the elastic energy is seen in its ultimate form in the effect of soft elasticity [7,8], when a stretched nematic rubber may reduce its effective modulus (the slope of a stress-strain curve) to zero by optimising the director rotation and associated shear strains.

Distortions in a cholesteric elastomer cannot be soft because of elastic compatibility constraints in matching different director and shear modes along the helix. If the director at a position z rotates towards the x axis, it is known that the elongation λ_{xx}, contraction λ_{yy}, and shear λ_{xy} are precisely determined by the initial orientation, ϕ_0, and the rotation from it, if the process is to be soft. The next slab of material, at $z + dz$, has the initial orientation $\phi_0 + q_0 dz$ and a different set of soft strains $\underline{\underline{\lambda}}$ must arise. Material points at y translate to $\lambda_{yy}(z) \cdot y$ and $\lambda_{yy}(z + dz) \cdot y$ in the two neighboring slabs along the helix; that is, they differ by a relative displacement $(\partial\lambda_{yy}/\partial z)dz \cdot y$. There is thus a generated shear $\lambda_{yz} = (\partial\lambda_{yy}/\partial z) \cdot y$ that diverges as the linear y dimension of the sample. We accordingly assert that the transverse contractions are *uniform*. Such deformations, e.g., λ_{xx} and λ_{yy} for stretching along the helix axis z, case (ii), have to be equal by symmetry and, therefore, $\lambda_{xx} = \lambda_{yy} = 1/\sqrt{\lambda}$. In contrast, for stretching perpendicular to the helix, case (i), the transverse contractions λ_{zz} and λ_{yy} should not be symmetric since one of them is along and the other perpendicular to the coarse-grained principal axis of a helix z. Incompressibility maintains the relation $\lambda_{zz}\lambda_{yy} = 1/\lambda$.

(i) Transverse elongation $\lambda_{xx} = \lambda$.—We consider the strain tensor in the following form:

$$\underline{\underline{\lambda}} = \begin{pmatrix} \lambda & 0 & 0 \\ 0 & \lambda_{yy} & 0 \\ 0 & 0 & \lambda_{zz} \end{pmatrix}. \tag{4}$$

Although one expects the director rotation in the azimuthal plane xy (cf. Fig. 1), there are no associated shear strains. Such shears, $\lambda_{xy}(z)$ and $\lambda_{yx}(z)$, would both lead to elastic compatibility problems and we assume they are suppressed. The shears $\lambda_{xz}(z)$ and $\lambda_{xz}(z)$ are not subject to compatibility requirements. However, they should not appear on symmetry grounds, which is easily confirmed by direct minimization. Now $\mathbf{n}_0 = \{\cos\phi_0, \sin\phi_0, 0\}$ and the rotated director after deformation is $\mathbf{n} = \{\cos\phi, \sin\phi, 0\}$. Note that the helix is $\phi_0 = q_0 z$ in the initial undistorted material. After deformation, because of the uniform affine contraction λ_{zz}, the material frame shrinks and the effective helical pitch becomes $\tilde{q} = q_0/\lambda_{zz}$ in all expressions below. With the $\underline{\underline{\ell}}_0$ and $\underline{\underline{\ell}}$ implied by these $\mathbf{n}_0$ and $\mathbf{n}$, the free energy density Eq. (2) yields

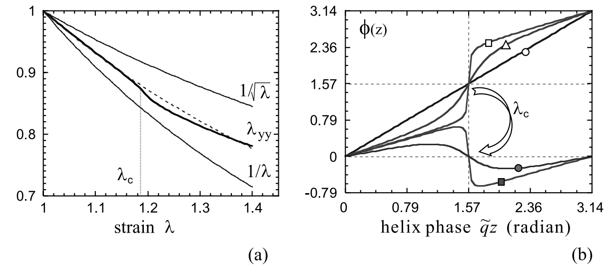
$$\begin{aligned} F_\perp = \frac{1}{2}\mu\{\lambda^2 + \lambda_{yy}^2 + \lambda_{zz}^2 + \frac{r-1}{r} \\ \times [\lambda^2(rc_0^2 s^2 - c^2 s_0^2) + \lambda_{yy}^2(rc^2 s_0^2 - s^2 c_0^2) \\ - 2\lambda\lambda_{yy}(r-1)s_0 c_0 sc]\}, \end{aligned} \tag{5}$$

where c_0 and s_0 are shorthand for $\cos\phi_0$ and $\sin\phi_0$, respectively; analogously, c and s stand for $\cos\phi$ and $\sin\phi$. The appearance of terms linear and quadratic in ϕ (or rather $\sin\phi$ because all values of the azimuthal angle will be found along the cholesteric helix) indicate that rotations can always lower the energy for $\lambda \neq 1$. Minimization of $F_\perp$ with respect to ϕ results in the expression for the local director angle $\phi(z)$ at a given imposed extension λ, depending on the phase of cholesteric helix:

$$\tan 2\phi = \frac{2\lambda\lambda_{yy}(r-1)\sin 2\tilde{q}z}{(r-1)(\lambda^2+\lambda_{yy}^2)\cos 2\tilde{q}z + (r+1)(\lambda^2-\lambda_{yy}^2)} . \tag{6}$$

Substituting this oscillating expression back into $F_\perp$ and coarse graining it over the helix, we obtain the optimal magnitude for the transverse contractions along the pitch, λ_{zz}, and in the azimuthal plane, λ_{yy}, the latter plotted in Fig. 2(a). This variation is contrasted with two classical regimes—an isotropic 3D contraction $\sim 1/\sqrt{\lambda}$ and a 2D version $\sim 1/\lambda$, corresponding to $\lambda_{zz} = 1$. From the plot it is apparent that a good interpolation of the region below the threshold is achieved by a power law $\lambda_{yy} \simeq \lambda^{-3/4}$ (and, as a consequence, $\lambda_z \simeq \lambda^{-1/4}$). At a critical value $\lambda_c \simeq r^{2/7}$ a discontinuous jump in the director angle occurs; see Fig. 2(b) and also the kink in λ_{yy}, Fig. 2(a).

Initially, all directors at $0 < \tilde{q}z < \pi/2$ are induced to rotate "backward" towards $\phi = 0$, and all directors at $-\pi/2 < \tilde{q}z < 0$ rotate "forward" towards $\phi = \pi$, as the imposed deformation λ increases; see Fig. 2(b). Although $\phi = 0$ and π describe equivalent directors, the twist wall between these two states becomes more and more sharp. Because of the helix imprinting, the orientations $\phi = 0$ at $\tilde{q}z = 0$ and $\phi = \pi$ at $\tilde{q}z = \pi$ are pinned, as is the middle point of the twist wall at $\tilde{q}z = \pi/2$. As a result, no change of the helical pitch can occur. This is in contrast with cholesteric liquid crystals, where in a classical problem of helix unwinding by an electric or a magnetic field one finds an increase in cholesteric pitch [5,9] along with the coarsening of the helix.



(a) (b)

FIG. 2. (a) The transverse contraction, λ_{yy}, as a function of imposed $\lambda_{xx} = \lambda$. Solid line shows the exact numerical solution of the coarse-graining problem for $r = 1.9$; one can see the kink where the discontinuous transition at $\lambda_c = r^{2/7} \approx 1.2$ takes place. The dashed line is an interpolation by $\lambda_{yy} = \lambda^{-3/4}$; two thin lines show classical regimes of $\lambda_{yy} = 1/\sqrt{\lambda}$ and $1/\lambda$. (b) The director angle ϕ against the cholesteric helix phase $q_0 z$ for increasing strain λ = 1 (open circle), 1.15 (triangle), 1.23 (open square), 1.25 (shaded square), and 1.5 (shaded circle). At $\lambda \geq \lambda_c$ the director pinning at $\phi = \pi/2$ breaks down and a discontinuous transition occurs, after which the director continuously rotates towards the final uniform $\phi = 0$.

Examining Eq. (6) one finds that as the increasing applied strain reaches a critical value λ_c, the width of the twist wall, centered at $\tilde{q}z = \pi/2$ between the values $\phi = \pi/4$ and $3\pi/4$, decreases to zero and the discontinuous transition occurs. The director in the midpoint of the wall breaks away from the pinning and jumps from $\phi = \pi/2$ to $\phi = 0$, along the strain axis, thus removing the topologically constrained twist wall. From this point there is no barrier for director rotation towards the final uniform orientation with $\phi = 0$, as the last two curves in Fig. 2(b) indicate.

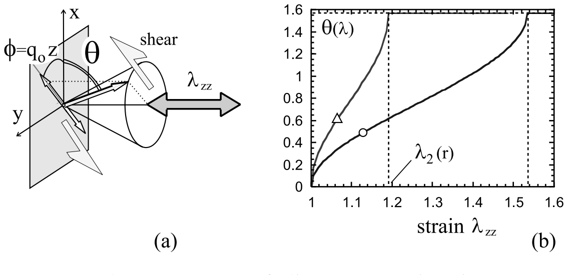
A discontinuous director jump at a critical strain has been predicted and indeed observed in nematic elastomers stretched at exactly 90° to their initial director $\mathbf{n}_0$ [7,10]. In a stretched cholesteric, one always finds an exact phase angle $\phi = \pi/2$ along the helix, where the center of the narrowing twist wall becomes pinned from both sides. It is this point that experiences a discontinuous jump.

(ii) Stretching along the pitch axis $\lambda_{zz} = \lambda$.—We now take (cf. Fig. 1)

$$\underline{\underline{\lambda}} = \begin{pmatrix} 1/\sqrt{\lambda} & 0 & \lambda_{xz} \\ 0 & 1/\sqrt{\lambda} & \lambda_{yz} \\ 0 & 0 & \lambda \end{pmatrix} . \tag{7}$$

No compatibility problem with shears $\lambda_{xz}(z)$ and $\lambda_{yz}(z)$ arises from their variation with z along the helical pitch. By contrast, their conjugate strains λ_{zx} and λ_{zy}, which would also have to vary with z, would lead to a serious compatibility mismatch, e.g., $\partial\lambda_{zx}/\partial z = \partial\lambda_{zz}/\partial x$. We therefore assume λ_{zx} and λ_{zy} are suppressed even though in other settings [7] these are the generators of soft elastic response.

In this geometry one expects the director rotation out of the azimuthal xy plane; see Fig. 3(a). The initial director is, as before, $\mathbf{n}_0 = \{\cos q_0 z, \sin q_0 z, 0\}$, while after deformation the rotated director is $\mathbf{n} = \{\cos\theta \cos\tilde{q}z, \cos\theta \sin\tilde{q}z, \sin\theta\}$. As in the case (i), all physical dimensions in the deformed sample are scaled by the affine strain. In particular, here $z \to \lambda z$, resulting in the corresponding



(a) (b)

FIG. 3. (a) The geometry of director rotation in response to stretching λ_{zz} along the helix axis. (b) The angle θ of director tilt plotted against the imposed strain λ, Eq. (11) for $r = 1.3$ (triangle) and $r = 1.9$ (circle). Strain varies from 1 to $\lambda_2 = r^{2/3}$ at which point the alignment is $\theta = \pi/2$, uniformly along the former pitch axis.

expansion of the cholesteric pitch: $\tilde{q} = q_0/\lambda$. With the $\underline{\underline{\ell}}_0$ and $\underline{\underline{\ell}}$ defined by the axes $\mathbf{n}_0$ and $\mathbf{n}$, the free energy density Eq. (2) now becomes a function of three variables: the director tilt angle θ and the two shear strains $\lambda_{xz}(z)$ and $\lambda_{yz}(z)$ (we continue to neglect the effects of director gradients and Frank elasticity). Algebraic minimization over these components of strain tensor is not difficult and results in

$$\begin{pmatrix} \lambda_{xz} \\ \lambda_{yz} \end{pmatrix} = \lambda \frac{(r-1)\sin 2\theta}{r+1-(r-1)\cos 2\theta} \begin{pmatrix} \cos\tilde{q}z \\ \sin\tilde{q}z \end{pmatrix}, \tag{8}$$

in phase with the azimuthal angle along the helical pitch. Equation (8) describes small distortions in the xy plane, perpendicular to the helix axis, rotating following the initial orientation $\mathbf{n}_0$. On substitution of these optimal shears back into the free energy density one obtains

$$F_\parallel = \frac{1}{2}\mu\left[\frac{\lambda^2}{1+(r-1)\sin^2\theta} + \frac{2+(r-1)\sin^2\theta}{\lambda}\right]. \tag{9}$$

$F_\parallel$ expands at small tilt angle θ as

$$F_\parallel \approx \frac{1}{2}\mu(\lambda^2 + 2/\lambda) - \frac{1}{2}\mu\theta^2(r-1)(\lambda^2 - 1/\lambda), \tag{10}$$

that is, the director starts to rotate down to define a cone of semiangle $\pi/2 - \theta$ immediately as the strain $\lambda > 1$ is imposed. The equilibrium director tilt is obtained by minimization of the full free energy density $F_\parallel(\theta)$:

$$\sin^2\theta = \frac{\lambda^{3/2} - 1}{r-1}; \qquad \theta = \arcsin\sqrt{\frac{\lambda^{3/2} - 1}{r-1}}. \tag{11}$$

The director rotation starts and ends in a characteristically singular fashion Fig. 3(b) (reminiscent of the universal optomechanical response seen in nematic elastomers [11]). The rotation is complete with the director aligned along the extension axis ($\theta = \pi/2$) at $\lambda = r^{2/3}$ which, for some elastomers, can be a very large extension.

In contrast to conventional cholesteric liquid crystals, we have altogether ignored effects of Frank elastic energy. The most compelling evidence for this is the very stability of the imprinted helical state in the face of the Frank penalty $\frac{1}{2}K_2 q_0^2$. The argument for this relies upon the great difference in characteristic length scales, the elastomer penetration depth, more accurately expressed as ξ [cf. Eq. (3)], and the director modulation wavelength estimated by the helical pitch $p = \pi/q_0 \gg \xi$. There are two possibilities to alter this inequality—by increasing the penetration depth ξ (by either making a weaker gel or a less anisotropic one) or by locally increasing the director gradient (e.g., in the ever narrowing twist wall, Fig. 2). As the width of the twist wall decreases to zero, the Frank energy density grows and diverges at the critical strain λ_c. Therefore, the local analysis of Eqs. (5) and (6) is valid only outside the region of strain $\Delta\lambda \sim (q_0\xi)^2$ around λ_c. In a typical hard nematic rubber this is a very small deviation, not altering the conclusions drawn for the case (i), but in a weak gel with low chain anisotropy it may become more substantial. Also, the actual finite width of the twist wall at the transition may raise the question of topological mechanism for eliminating the twist stored in the cholesteric helix, perhaps by a disclination loop expansion in the xy plane.

One can estimate how weak a gel must be for the Frank elasticity to intervene in our analysis in a more substantial way. When $\xi \sim p$, for example, with a pitch $p \sim 4 \times 10^{-7}$ m, then a rubber modulus of only $\mu \sim 60$ J/m^3 is required (assuming $[r-1] \sim 1$). Nematic elastomers typically have $\mu \sim 10^3 - 10^5$ J/m^3 and their cholesteric analogs would clearly find Frank elastic effects minor. However, an elastomer with a reasonable $\mu \sim 10^3$ J/m^3 would feel the director gradients when its polymer chain anisotropy becomes as low as $r = \ell_\parallel/\ell_\perp \sim 1.25$. Such a value is easily reached in side-chain liquid crystal polymers, especially near the clearing point [7].

To summarize, we have predicted a qualitatively new response of an elastomer with chiral cholesteric microstructure to applied fields that is different from classical cholesteric liquids. Likewise, the chiral imprinting and its modification by elastic fields is a new effect in rubbers and solids. One could envisage tuning these effects by the use of solvents (with or without chiral power) and by other fields affecting the director, for instance electric.

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